REMARKS

Applicants and the undersigned reviewed the pending Office Action carefully. Reconsideration is respectfully requested. Nonetheless, in light of the positions presented herein, this application is believed to be in condition for allowance.

Several claims were rejected under 35 U.S.C. § 112, second paragraph as indefinite. Responsive thereto, the preambles of claims 12 and 13 are hereby amended solely for purpose of clarification, without further limitation or prior art concern.

Several claims were rejected under 35 U.S.C. § 102(e) as being anticipated by Dubertret. Again, Applicants appreciate the Examiner's concern, but for reasons previously presented believe Dubertret to have been misconstrued. Nonetheless, Applicants completed the invention claimed in the present application before the effective date of the Dubertret reference. More particularly, the invention recited in independent claims 1, 14 and 20 was conceived and with due diligence reduced to practice prior to the effective date of the Dubertret reference. Such prior invention was previously supported, pursuant to 37 CFR § 1.131, by the declaration of co-inventor Habib Skaff and incorporated copies of pages from his laboratory research notebook. Such prior invention is now further supported by the corresponding declaration of co-inventor Todd S. Emrick, also incorporating copies of the aforementioned Skaff laboratory research notebook pages witnessed by Mr. Emrick. (A copy of the Emrick declaration is hereby provided, together with Exhibit A. The original executed declaration is available upon Examiner request.)

Several claims were rejected under 35 U.S.C. § 102(a) as anticipated by Billancia. As would be understood by those skilled in the art, terpyridine ligands provide "tridentate" coordination with respect to a corresponding metal center. Such coordination is illustrated in Billancia and further supported by co-author Schubert in a related publication, attached hereto as Exhibit B, in contrast to a monodentate nitrogenous

moiety recited in claim 1. Support for such clarification can be found throughout the present specification, as would be understood by those skilled in the art with an understanding of Billancia/Schubert. In particular, reference is made to Figures 2 and 4 of the present specification.

As such, Billancia does not anticipate Applicants' nitrogenous coupling moiety. The rejection should be withdrawn, with the subject claims allowed to proceed toward issue.

Several claims were rejected under 35 U.S.C. § 102(e) as anticipated by Ekwuribe. Again, Applicants appreciate the Examiner's concern, but respectfully disagree. The cited Ekwuribe compounds do not comprise a pyridine ligand. Rather, the substitution pattern employed by Ekwuribe is inapposite to Applicants' invention. The resulting positive-charged pyridinium ion is not pyridine, and, as understood in the art, such compounds could not be pyridine ligands. As such, Ekwuribe does not anticipate Applicants' polymeric compound. This rejection should also be withdrawn, with the subject claims allowed to proceed toward issue.

This application is now believed to be in condition for allowance. Consistent therewith, favorable action is respectfully requested. The Examiner is invited to contact the undersigned by telephone should any issue remain. Thank you for your help and consideration.

Respectfully submitted:
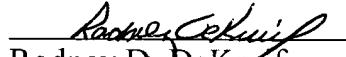
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Full Paper: Poly(ethylene oxide) of various molecular weights ($\bar{M}_n = 3\,000$, $5\,200$, $10\,000$, $16\,500$ g · mol^{-1}) has been modified with terpyridine end groups as building blocks for water-soluble metallo-supramolecular polymers. Metallo-supramolecular A–A homopolymers have been prepared and characterized by complexing the terpyridine units of one selected poly(ethylene oxide) ($\bar{M}_n = 3\,000$ g · mol^{-1}) with the following transition metal ions in their 2+ oxidation state: Fe, Ru, Co, Ni, Cu, Zn, and Cd. In addition, the stability of the supramolecular connection with respect to pH variations has been investigated.
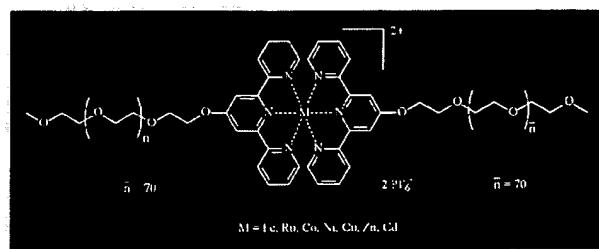
Schematic representation of the product of poly(ethylene oxide) modification with terpyridine end groups and the metal complexation.

Water-Soluble Building Blocks for Terpyridine-Containing Supramolecular Polymers: Synthesis, Complexation, and pH Stability Studies of Poly(ethylene oxide) Moieties[a]

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Introduction

Supramolecular chemistry offers the possibility of selectively constructing large multicomponent architectures through secondary interactions. Due to the fact that these interactions are in general weaker than covalent bonds, they can easily be addressed by external factors such as pH, temperature, solvent, redox processes, and shear forces.[1] Recently, principles and binding moieties from supramolecular chemistry have been successfully introduced and applied in the field of polymer chemistry. The major objective is to obtain materials that combine the special features from both fields: the intrinsic material properties arising from the polymer backbone in combination with the self-assembly, switching and/or reversibility properties of the supramolecular entities that are connected to the polymer backbone. Examples from literature involve hydrogen bonding, π–π stacking and metal-ligand interactions.[2] Recently, we have introduced a metal-ligand complex as a supramolecular linker between two polymers in order to selectively obtain homo- as well as block copolymers.[3] This linker consists of two 2,2':6',2''-terpyridine-ligands that chelate around a ruthenium(II) ion in an octahedral fashion. Terpyridine is known to form stable *bis*-complexes with a wide range of transition metal ions.[4,5] Polymers can easily be introduced at the 4'-position of the ligand by a nucleophilic substitution reaction. We have successfully attached, for example, polystyrene, poly(ethylene-*co*-butylene) and a short poly(ethylene oxide).[3,6] Applying the latter polymer as building block for amphiphilic metallo-supramolecular block copolymers, highly interesting new nanomaterials could be obtained. By first preparing micelles and subsequent breaking of the metal complex it was possible to obtain defined functional nano-objects.[7] To expand the possibilities for preparing such materials, we have prepared water-soluble terpyridine

end-functionalized poly(ethylene oxide)s ($\overline{M}_n = 3\,000$, 5 200, 10 000 and 16 500 $g \cdot mol^{-1}$). The terpyridine end-functionalized polymer with $\overline{M}_n = 3\,200$ $g \cdot mol^{-1}$ was utilized for the formation of terpyridine-metal complexes with a variety of transition metal ions (Fe, Ru, Co, Ni, Cu, Zn, and Cd) in the 2+ oxidation state (Scheme 1). In addition, first studies regarding the stability of the metallo-supramolecular polymers with respect to pH variations were performed, revealing that some systems could be opened by means of pH. Other methods to address such polymer complexes may involve temperature, competitive ligands for coordination of the metal ion, shear forces, extended exposure to UV light, or electrochemical methods, see e.g. reference [8].

Experimental Part

Chemicals were received from Aldrich, Fluka, and Polymer-source, as well as Shearwater, and used without further purification. Solvents were bought from Biosolve. Dimethyl sulfoxide (DMSO) was dried over BaO. For preparative size exclusion chromatography, Bio-Rad SX-1 Beads swollen in CH_2Cl_2 were used. ^1H NMR and ^{13}C NMR were recorded on a Varian Inova spectrometer with frequencies of 500 and 125 MHz respectively, and on a Varian Mercury spectrometer with frequencies of 400 and 100 MHz at 25 °C. Chemical shifts are given in ppm downfield from TMS. UV/Vis spectra were

recorded on a Perkin Elmer Lambda 45P spectrophotometer. Matrix assisted laser desorption/ionization mass spectra were obtained, using dithranol as the matrix, and NaI, on a PerSeptive Biosystems Voyager DE PRO spectrometer using a layer-by-layer spotting technique. Size exclusion chromatography was performed on a 30 cm long Waters Styragel HT4 column and analyzed with an RI detector (Waters 1414) with chloroform as the eluent and 4 vol.-% Et_3N and 2 vol.-% 2-propanol as additives to reduce column interactions, at a flow of 0.5 mL $\cdot$ min^{-1} utilizing a Waters 1515 pump. Poly(ethylene oxide) standards were used for calibration. IR spectra were measured on a Perkin Elmer 1600 FTIR in ATR mode. Buffer solutions (500 mL) were prepared from FIXANAL® buffer concentrate for pH 1.00, 3.00, 5.00, 7.00, 10.00, and 13.00 at $T = 20$ °C.

General Procedure for the Synthesis of Terpyridine End-Functionalized Poly(ethylene oxide)

Powdered KOH and α-methoxy-ω-hydroxy-poly(ethylene oxide) (with $\overline{M}_n = 3\,000, 5\,200, 10\,000, 16\,500$ $g \cdot mol^{-1}$) were stirred under argon in dry DMSO at 70 °C. After 30 minutes a two times excess of 4'-chloro-2,2':6',2''-terpyridine[9] was added. The mixture was stirred for 24 h, then poured into cold water and extracted with CH_2Cl_2. The combined organic layers were dried over Na_2SO_4 and removed in vacuo. The compounds were purified by preparative size exclusion chromatography (BioBeads SX-1, CH_2Cl_2), followed by a double
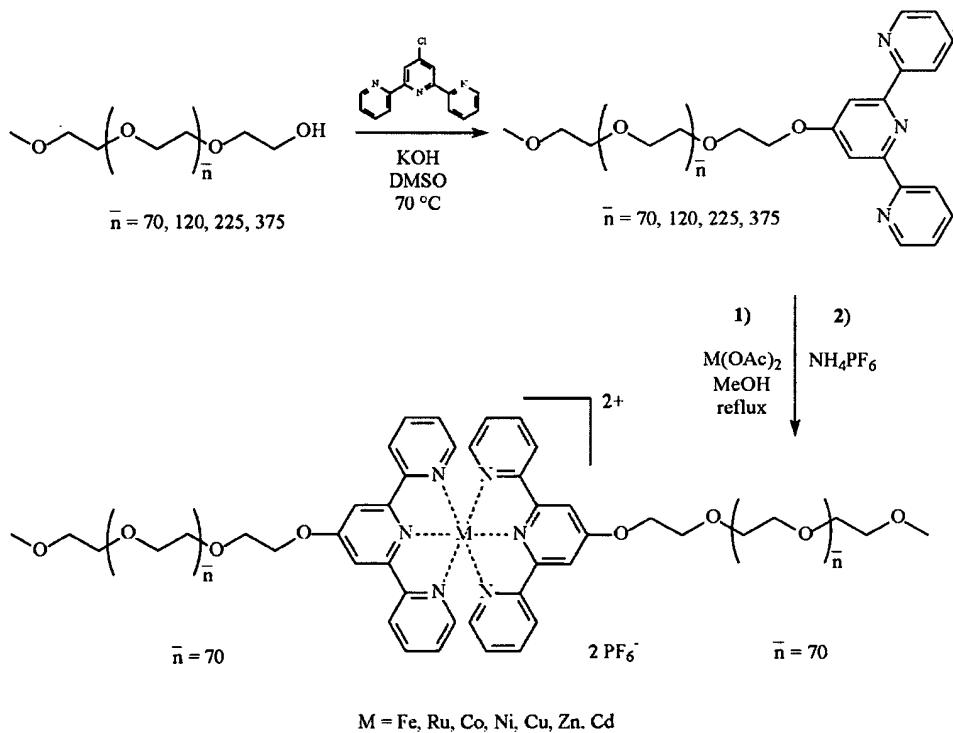
Scheme 1. Schematic representation of the poly(ethylene oxide) modification with terpyridine end groups and the metal complexation to PEO_{70}-[M]-PEO_{70}.

precipitation from tetrahydrofuran (THF) into diethyl ether. The products are designated **1, 2, 3** and **4** for PEO_{70}, PEO_{120}, PEO_{225}, and PEO_{375}, respectively.

^{1}H NMR (CDCl$_3$) (**1–4**): $\delta = 8.68$ (dt, H^6;H$^{6''}$), 8.61 (dt, H^3;H$^{3''}$), 8.04 (s, H$^{3'}$;H$^{5'}$), 7.85 (td, H^4;H$^{4''}$), 7.34 (ddd, H^5;H$^{5''}$), 4.40 (t, tpyOCH$_2$), 3.93 (t, tpyOCH$_2$CH$_2$), 3.83–3.45 (m, PEO backbone), 3.38 (s, OCH$_3$).

^{13}C NMR (CDCl$_3$) (**1–4**): $\delta = 166.6$ (C$^{4'}$), 156.7 (C$^{2'}$, C$^{6'}$), 155.6 (C^2, C$^{2''}$), 148.7 (C^6, C$^{6''}$), 136.4 (C^4, C$^{4''}$), 123.5 (C^5, C$^{5''}$), 120.9 (C^3, C$^{3''}$), 107.0 (C$^{3'}$, C$^{5'}$), 72.2–67.4 (C PEO backbone), 58.6 (OCH$_3$).

UV/Vis (H$_2$O) (**1–4**): λ_{max} (ε) = 278 (13 200), 234 (17 000).

IR (ATR) (**1–4**): 2 884, 2 741, 1 601, 1 583, 1 565, 1 467, 1 455, 1 408, 1 360, 1 341, 1 279, 1 241, 1 205, 1 147, 1 101, 1 060, 992, 957, 947, 841, 797, 747, 736, 699, 659.

MALDI-TOF-MS (**1**): $\bar{M}_n = 3\,123$; (**2**) $\bar{M}_n = 5\,202$; (**3**) $\bar{M}_n = 10\,901$; (**4**) $\bar{M}_n = 17\,434$ g · mol^{-1}.

GPC (RI) (**1**): $\bar{M}_n = 2\,500$, PDI = 1.04; (**2**) $\bar{M}_n = 4\,200$, PDI = 1.09; (**3**) $\bar{M}_n = 10\,000$, PDI = 1.06; (**4**) $\bar{M}_n = 15\,500$, PDI = 1.04.

General Procedure for the Synthesis of PEO$_{70}$-[M]-PEO$_{70}$

The terpyridine-functionalized poly(ethylene oxide) (0.250 g) and the metal salt M(OAc)$_2$ × H$_2$O (M = Fe, Co, Ni, Cu, Zn, Cd; 0 < x < 4) in a molar ratio of 2:1 were stirred under reflux in 10 mL of MeOH for at least 4 hours. The reaction was followed by UV/Vis: when no more changes were observed in the UV spectrum, NH$_4$PF$_6$ (0.120 g, 0.73 mmol, 10-fold excess) was added to the solution. Stirring was continued for another 15 minutes, after which the reaction mixture was cooled to room temperature and partitioned between dichloromethane (50 mL) and water (25 mL). The organic layer was washed 3 times to remove excess salts, then dried over Na$_2$SO$_4$ and removed in vacuo. From the resulting solid a ^{1}H NMR spectrum was recorded. If uncomplexed starting polymer was present (deduced from the singlet at 8.0 ppm in ^{1}H NMR), preparative size exclusion chromatography was carried out (BioBeads SX-1, CH$_2$Cl$_2$). Finally, the metallo-supramolecular polymer was precipitated from THF into diethyl ether, filtered and dried for 2 days in a vacuum stove at 40 °C. Yields varied from 64 to 87%. Selected analytical data:

PEO-[Fe]-PEO (**5**)

^{1}H NMR (CD$_3$CN): $\delta = 8.57$ (s, H$^{3'}$;H$^{5'}$), 8.51 (d, H^3;H$^{3''}$), 7.93 (ddd, H^4;H$^{4''}$), 7.20 (d, H^6;H$^{6''}$), 7.12 (ddd, H^5;H$^{5''}$), 4.80 (t, tpyOCH$_2$), 4.14 (4H, t, tpyOCH$_2$CH$_2$), 3.83–3.39 (m, PEO backbone), 3.34 (s, OCH$_3$).

UV/Vis (H$_2$O): λ (ε): 556 (8 400), shoulder at 506 (5 700), 361 (5 300), 315 (31 000), 271 (39 200), 245 (39 200).

IR (ATR): 2 883, 2 714, 1 616, 1 563, 1 551, 1 467, 1 455, 1 425, 1 414, 1 360, 1 342, 1 280, 1 241, 1 147, 1 099, 1 060, 961, 947, 840, 793, 758, 731, 699, 665.

PEO-[Co]-PEO (**6**)

^{1}H NMR (CD$_3$CN): $\delta = 111.12$, 74.22, 70.17, 34.52, 14.93, 9.35, 7.13 6.07, 5.22, 4.73, 4.35–3.36, 3.35.

UV/Vis (H$_2$O): λ (ε): 453 (730), 306 (22 600), 272 (40 800), 241 (43 300).

IR (ATR): 2 883, 2 741, 1 615, 1 572, 1 560, 1 467, 1 455, 1 360, 1 342, 1 280, 1 241, 1 146, 1 099, 1 060, 961, 947, 839, 797, 751, 730, 700, 661.

PEO-[Zn]-PEO (**7**)

^{1}H NMR (CD$_3$CN): $\delta = 8.62$ (d, H^3;H$^{3''}$), 8.31 (s, H$^{3'}$;H$^{5'}$), 8.20 (ddd, H^4;H$^{4''}$), 7.81 (d, H^6;H$^{6''}$), 7.44 (ddd, H^5;H$^{5''}$), 4.74 (t, tpyOCH$_2$), 4.08 (4H, t, tpyOCH$_2$CH$_2$), 3.80–3.43 (m, PEO backbone), 3.35 (s, OCH$_3$).

UV/Vis (H$_2$O): λ (ε): 322 (28 800), 309 (26 500), 273 (38 100), 243 (53 900).

IR (ATR): 2 883, 2 742, 1 614, 1 603, 1 575, 1 563, 1 467, 1 455, 1 342, 1 279, 1 241, 1 147, 1 098, 1 060, 961, 840, 798, 750, 731, 700, 661.

PEO-[Cd]-PEO (**8**)

^{1}H NMR (CD$_3$CN): $\delta = 8.63$ (d, H^3;H$^{3''}$), 8.23 (s, H$^{3'}$;H$^{5'}$), 8.22 (ddd, H^4;H$^{4''}$), 8.06 (broad, H^6;H$^{6''}$), 7.52 (ddd, H^5;H$^{5''}$), 4.69 (t, tpyOCH$_2$), 4.06 (t, tpyOCH$_2$CH$_2$), 3.82–3.49 (m, PEO backbone), 3.39 (s, OCH$_3$).

UV/Vis (H$_2$O): λ (ε): 320 (21 200), 309 (22 900), 274 (37 100), 242 (52 500).

IR (ATR): 2 883, 2 742, 1 611, 1 600, 1 575, 1 562, 1 467, 1 455, 1 360, 1 342, 1 279, 1 241, 1 147, 1 099, 1 060, 961, 840, 797, 748, 729, 700, 660.

PEO-[Ni]-PEO (**9**)

UV/Vis (H$_2$O): λ (ε): 324 (16 700), 311 (20 400), 299 (19 700), 273 (41 000), 243 (43 000).

IR (ATR): 2 883, 2 742, 2 695, 1 614, 1 604, 1 573, 1 563, 1 467, 1 456, 1 360, 1 342, 1 280, 1 241, 1 146, 1 099, 1 060, 962, 947, 840, 797, 751, 731, 700, 662.

PEO-[Cu]-PEO (**10**)

UV/Vis (H$_2$O): λ (ε): 329 (20 400), 316 (21 400), 275 (44 700), 251 (45 300).

IR (ATR): 2 883, 2 742, 1 616, 1 574, 1 562, 1 467, 1 455, 1 360, 1 342, 1 279, 1 241, 1 146, 1 099, 1 060, 961, 947, 840, 797, 749, 728, 700, 662.

^{1}H NMR spectra of PEO-[Ni]-PEO **9** and PEO-[Cu]-PEO **10** did not show any peaks in the aromatic region, due to the paramagnetic nature of the metal complexes. Nevertheless, signals for uncomplexed terpyridine could not be observed.

PEO$_{70}$-[Ru]-PEO$_{70}$ was synthesized by a 2-step reaction via the mono complex of PEO$_{70}$-[RuCl$_3$] and characterized as described previously.[3]

Results and Discussion

The 2,2′:6′,2″-terpyridine moiety was successfully introduced at the chain end of monochelic poly(ethylene oxide) of various molecular weights ($\bar{M}_n = 3\,000$, 5 200, 10 000, 16 500 g · mol^{-1}) by utilization of an aromatic nucleophilic substitution reaction of 4′-chloroterpyridine with the hydroxy end group of the corresponding polymers.[3,6]

The ^{1}H NMR spectra of the purified products revealed in each case signals from the terpyridine ligand in the aromatic region. Of particular interest is the singlet attributed to the 3',5' protons on the middle ring, which has moved from 8.47 to 8.04 ppm due to the substitution from a chloro to an oxygen atom at the 4'-position. Also the methylene protons of the backbone next to the ligand have shifted from 3.83 for the hydroxy-substituted PEO to 4.40 and 3.93 for the terpyridine-substituted end group. MALDI-TOF-MS has proven to be an excellent tool for end-group analysis of these polymers.[10] In Figure 1 a clear shift of 232 Daltons can be observed for each single peak, which corresponds to the mass of the terpyridine-ligand, proving the successful and complete end group functionalization. The GPC traces (Figure 2) were recorded with an eluent consisting of 94% chloroform, 4% Et_3N and 2% 2-propanol. This mixture reduced most of the column interactions of the terpyridine end-functionalized polymers. Tailing of the GPC-traces, which can be observed when using pure chloroform or THF, leads to unreliable data regarding $\bar{M}_n$ and PDI. Nevertheless, the $\bar{M}_n$ of the lower molecular weight species are still somewhat low compared to the MALDI-TOF-MS and ^{1}H NMR data, and in comparison with the starting materials, which can be regarded as an effect of column interactions. For the higher molecular weight species, with a lower absolute terpyridine content, the molecular weights derived by these three independent techniques are comparable (Table 1), so for the higher $\bar{M}_n$ column interactions are negligible.

The terpyridine-functionalized PEO_{70} (**1**) was employed as a metallo-supramolecular linker between two polymer chains by complexation with Fe, Ru, Co, Ni, Cu, Zn and Cd ions, yielding PEO_{70}-[M]-PEO_{70} homopolymer complexes. A very slight excess of the metal ion was added to

Figure 2. GPC traces of poly(ethylene oxide) of various molecular weights with hydroxy end group (top) and after modification with terpyridine (bottom).

establish full complexation to the *bis*-complex. These systems were characterized by GPC, MALDI-TOF-MS, UV/Vis, FTIR and ^{1}H NMR for diamagnetic complexes (i.e. Fe, Ru, Zn and Cd). In these cases shifts for the singlet of 3',5' protons, for the 6,6" protons and for the methylene protons were observed (Figure 3). Due to the octahedral surrounding of the complex, the ligand protons in the 6,6"-position are located above the middle ring of the other terpyridine-ligand.[5] The paramagnetic Co complex revealed a Knight shift in ^{1}H NMR due to specific coupling of the electronic and nuclear spin, giving rise to proton shifts of up to 110 ppm from TMS.[11] The UV/Vis spectra of the metallo-supramolecular polymers are similar to model complexes synthesized before.[5] IR spectroscopy revealed a clear shift of the C=C and C=N stretch vibrations for the metal complexes compared to the free


Figure 1. MALDI-TOF mass spectra of poly(ethylene oxide) ($\overline{DP}$ = 120) with hydroxy end group (top) and after modification with terpyridine (bottom).

Table 1. Determination of the molecular weights of different poly(ethylene oxide) starting materials and the corresponding terpyridine-functionalized poly(ethylene oxide)s by three independent techniques; polydispersity indices ($\bar{M}_w/\bar{M}_n$) are given in parentheses.

	$\bar{M}_n$ (PDI) by GPC	$\bar{M}_n$ by ^{1}H NMR	$\bar{M}_n$ by MALDI-TOF MS
$PEO_{70}OH$	2 800 (1.04)	3 000	2 923
1	2 500 (1.04)	3 100	3 123
$PEO_{120}OH$	4 300 (1.06)	5 200	5 036
2	4 200 (1.09)	5 400	5 202
$PEO_{225}OH$	9 400 (1.04)	10 000	10 876
3	10 000 (1.06)	10 300	10 901
$PEO_{375}OH$	15 400 (1.04)	16 500	16 863
4	15 500 (1.04)	16 600	17 434

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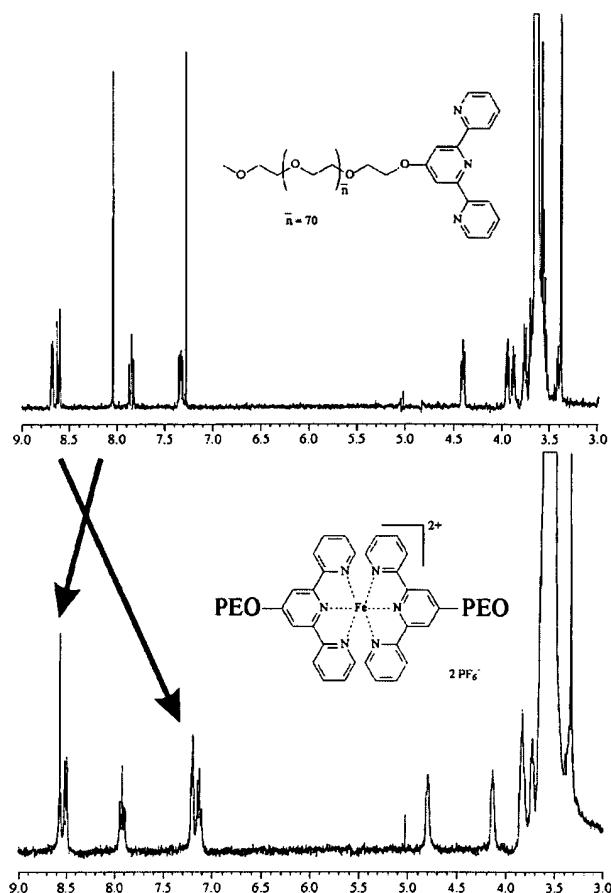
Figure 3. ^{1}H NMR spectra of poly(ethylene oxide) ($\overline{DP} = 70$) with free terpyridine end group (top) and its Fe^{II} complex (bottom) in CDCl$_3$ and CD$_3$CN, respectively. The arrows indicate the shifts of the respective protons. Most important are the shifts of the singlet of the H$^{3'}$:H$^{5'}$ protons from 8.04 to 8.57 ppm and the doublet of the H^6:H$^{6''}$ protons shifting from 8.68 to 7.20 ppm due to the different surroundings upon complexation.

Figure 4. IR spectra in the region 1750–1250 cm^{-1} for poly(ethylene oxide) ($\overline{DP} = 70$) of the free terpyridine end group and its Ni^{II} complex.

The stability of the different metallo-supramolecular connecting units regarding pH variations was investigated in detail by varying the pH. First, the polymers were solubilized in different pH-buffers (pH = 1.0, 3.0, 5.0, 7.0, 10.0, and 13.0) and investigated by UV/Vis spectroscopy. The bands of interest are the metal-to-ligand-charge-transfer (MLCT) bands for the Fe- and Ru-containing polymers at 556 and 486 nm respectively and the ligand-centered $\pi-\pi^*$ bands for all metal ions, roughly between 290 and 330 nm. The absorptions in this region are attributed to the rotation of the outer pyridine rings along the central C–C bonds that connect them. The difference in the spectra of the respective metal complexes in this region arises mostly from the different electronic interactions induced by the metal ion and, related to the previous statement, from distortions from ideal octahedral geometry. Figure 5 shows the behavior of the metallo-supramolecular polymers in the different pH-buffers. The first finding to be noted is that the metal complexes containing Fe, Co, Zn and Cd are sensitive to high and low pH (Figure 5b and 5c, respectively). At these pH-values, the UV/Vis spectrum of the polymer resembles that of the free or protonated ligand. In contrast to these findings it can clearly be seen that the ruthenium-, nickel- and copper complex are insensitive to changes in pH over a wide range (1–13) (Figure 5d–f). In time, however, the copper complex is slowly opened up in acidic media. The polymers containing nickel and ruthenium do not show any changes in the UV/Vis spectra in both basic and acidic solution, even after prolonged periods of time (typically days). These findings are in good agreement with model systems and reported data in literature, and demonstrates the stability of these complexes.[14] It was possible to regenerate the starting material with the free ligand: the iron-containing polymer was subjected to a 1 M NaOH solution. After the colour had faded away, the basic water layer was extracted with dichloromethane, dried over

ligand (region between 1 650 and 1 550 cm^{-1}) (Figure 4). From these investigations complete complex formation can be assumed. Using a standard GPC set-up, a breakage of the complex could be observed through shear forces and interaction with the column material (see also reference [12]). In MALDI-TOF-MS breakage occurred due to the relatively high energy required to ionize and desorb the polymers. By tuning the solvent and the flow rate in GPC (thus reducing the interactions and the amount of shear) the ratio of metal complex to free ligand could be increased, but a successful GPC set-up remains a challenge. These observations are valid for different materials like polystyrene homo dimers as well. By reducing the laser intensity in MALDI-TOF-MS, the ratio of metal complex to free ligand could also be increased. We are currently trying to relate these observations to binding strengths and stabilities of these metal complexes and model systems.[13]

Figure 5.   UV/Vis spectra of the metallo-supramolecular polymers in different buffer solutions: a) PEO$_{70}$-[M]-PEO$_{70}$ at pH = 7.0; b) PEO$_{70}$-[M]-PEO$_{70}$ at pH = 1.0; c) PEO$_{70}$-[M]-PEO$_{70}$ at pH = 13.0; d) Ru; e) Ni; f) Cu.

Na$_2$SO$_4$ and removed in vacuo. The ^{1}H NMR, UV, and GPC data of the resulting white residue are similar to those described in the experimental section for 1, and prove that the uncomplexed polymer could be regenerated.

Conclusion

We have reported the synthesis and characterization of terpyridine end-functionalized poly(ethylene oxide)s of various molecular weights, increasing the number of available water-soluble building blocks for metallo-supramolecular homo and block copolymers. It was possible to construct A–A homopolymers using Fe, Ru, Co, Ni, Cu, Zn, and Cd metal ions. These metal complexes were shown to act as pH-sensitive connection points. It was demonstrated that at high and low pH (13 and 1 respectively), the Fe-, Co-, Zn- and Cd-containing polymers can be de-complexed; the Cu system opens only at low pH after

extended periods of time. In contrast to these findings, the Ru- and Ni-containing polymers were completely insensitive to changes in pH. These results demonstrate that the metal complexes can be addressed by means of pH and thereby the material properties can be tuned by external stimuli. This will be of great importance for the development of "smart" materials and functional nanomaterials.

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PATENT

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re application of: Emrick et al.   )
)
Serial No: 10/643,015   )
) Attorney Docket No. 7163
)
Filed: August 18, 2003   )
)
For: PYRIDINE AND   )
          RELATED LIGAND   )
          COMPOUNDS,   )
          FUNCTIONALIZED   )
          NANOPARTICULATE   )
          COMPOSITES AND   )
          METHODS OF   )
          PREPARATION   )

Commissioner for Patents
P.O. Box 1450
Alexandria, VA 22313-1450

RULE 131 DECLARATION OF TODD S. EMRICK

1.   I, Todd S. Emrick, am a co-inventor with regard to the invention (the "Invention") disclosed and claimed in the above-entitled application (the "Application"). I make this declaration in support of the Application and, in particular, to antedate a reference cited against the Application.

2.   The Invention claimed in the Application was completed before the effective date of application serial number 10/219,440 (*i.e.*, the Dubertret

reference). More specifically, the Invention was conceived and with due diligence reduced to practice prior to the effective date of the Dubertret reference.

3.   This Declaration, and prior invention, is supported by copies of pertinent pages from the laboratory research notebook of co-inventor Habib Skaff, signed and dated by Mr. Skaff, entries to which I contemporaneously witnessed. Date redacted copies of the aforementioned notebook pages are provided collectively as Exhibit A and incorporated herein by reference. These documents establish that the Invention was made at least as early as June 1, 2002, which is a date earlier than the effective date of the Dubertret reference.

I hereby declare that: All statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; that those statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under section 1001 of Title 18 of the United States Code; and that willful false statements may jeopardize the validity of the Application or any patent issuing thereon.

Date _12/28/2006_   _[signature]_
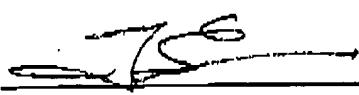
Todd S. Emrick

Exhibit A

Reagents

95 ① [phenol structure] OH ······ 2g , 0.022 mol

②
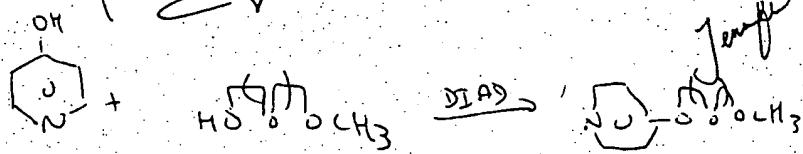
750 ③ m-PG 750 ······ 14.25g , 0.019 mol

262 ③ Ph₃P ······ 6.28g , 0.024 mol

212 ④ DIAD ······ 4.84g , 0.024 mol (4.72 mL)

⑤ THF (dry) ······ ~~300mL~~ 250 mL

Procedure

① Ph₃P + THF loaded into 2-neck flask & stirred under N₂ @ r.t.

② DIAD added via syringe & stirred for ½ hr.

③ "phenol" & alcohol added & stirred

④ reacted overnight

⑤ stripped off THF

⑥ added H_2O & ether → washed w/ ether

⑦ extracted product out w/ CH_2Cl_2 out of Aq phase → $MgSO_4$, Rotovac

→ NMR show some (R) → tryed redissolving in didn't work basic (.5M NaOH) solution & precipitating into CH_2Cl_2 (cold)

→ ran column eluting w/ CH_2Cl_2 : Et_2O : MeOH (7:3:0), (7:2:1)

Reagents

GS ① [N-O-OH] & 2g , 0.011mol
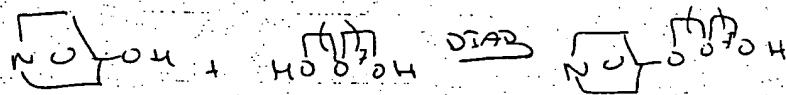
400
ρ=1.03
202 ② HO-O-O-OH   22g , 0.055mol
③ DIAD   2.63g , 2.55mL 0.013mol
262 ④ Ph₃P   3.41g , 0.03
⑤ ~~DIAD~~ THF (dry)   300mL

Procedure

① Ph₃P + THF loaded into 3-neck 500mL roundbottom
   ; stirred @ r.t under N₂

② DIAD added via syringe ; stirred for ½ hr.

③ phenol ; ~~acetate~~ diol added ; stirred

→ reacted over night

— rotevaped off all THF   → note

— extracted w/ H₂O → then aqueous washed
   w/ CH₂Cl₂ → too difficult to purify by column

→ rotevaped off CH₂Cl₂ → dissolved in H₂O,
   washed w/ ether, then Toluene → doesn't work well, so

→ try ~~acetifying~~ acidifying aqueous to make pyridine salt
   which will not be soluble in

Reagents
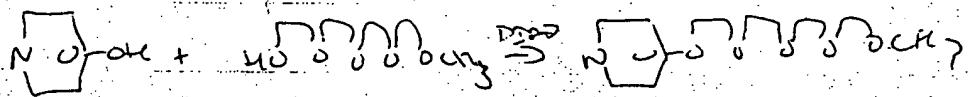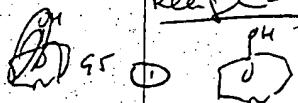
95	① (phenol)	5g,	0.055 g mol
128	② m-T-g	5.632g,	0.044 mol
~1.025 26 ~	③ Ph₃P	13.1g	0.05 mol
202	④ DEAD	10.1g,	0.05 mol, 9.85 mL
	⑤ THF (Dry)	~~400 mL~~ 400 mL	

Procedure

① Ph₃P ÷ THF loaded into 2-neck flask & stirred under N₂ @ r.t.

② DEAD added via syringe & stirred for ½ hr.

③ phenol ÷ alcohol added & stirred overnight

Reagents

95 ⓵ [pyrrolidinol structure]   4g , 0.042 mol
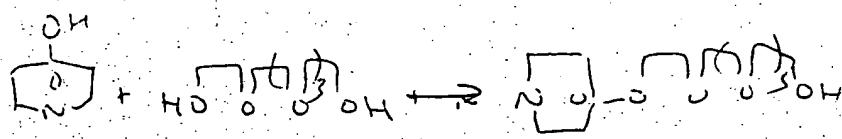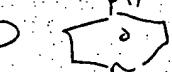
300 ② Heg   31.58g, 0.105 mol

262 ③ Ph_3P 13.1g   0.045 ~~0.05 mol~~

(~1.025) 202 ④ DIAD   10.1g,   0.05 mol, ~~10.35mL~~ 9.85mL

⑤ THF   500 mL

Procedure

① phenol, Ph_3P, DIAD, & THF loaded in 2-neck
& stirred @ r.t. under N_2 for ½ hr.

② diol added → stirred overnight

→ stripped of THF
→ crystd/CHCl3 ② CHCl3 : R (80:20) ③ CHCl3 : R : MeOH (75:20:5)
→ ran column elution w/ ① CHCl3 : R : MeOH (7:2:1)

→ tried distilling off unreacted diol @ 224°C @
@ 600 mtorr → didn't work well

→ ran column in CHCl3 : R : MeOH (78:20:2),
(75:20:5), (80:20:10)

Exchange to tri-monopyridinyl ester

Reagent

① pyridine NC ~40 mg
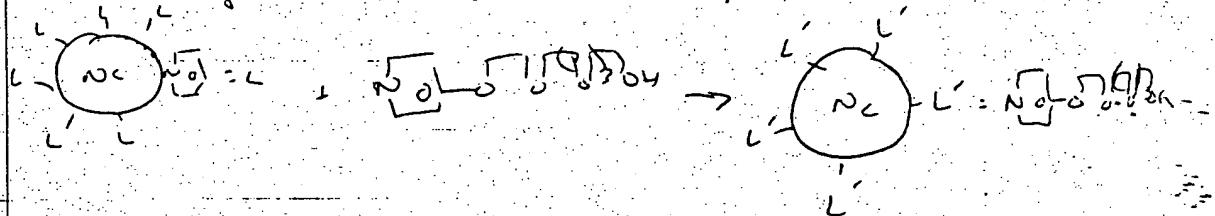
② [structure] 600 mg

③ THF (dry) 3 mL

④ DIW 6 mL

Procedure

A) ① 20 mg NC dispersed in solution of 300 mg
new ligand in THF → immediately went
into solution

② dried under N_2 flow and added 3 mL
DIW → most went into solution → centrifuged

B) ③ 20 mg NC dispersed in solution of 300 mg
new ligand in 3 mL DIW → NC went into
solution → centrifuged

Jennifer L. Smeed
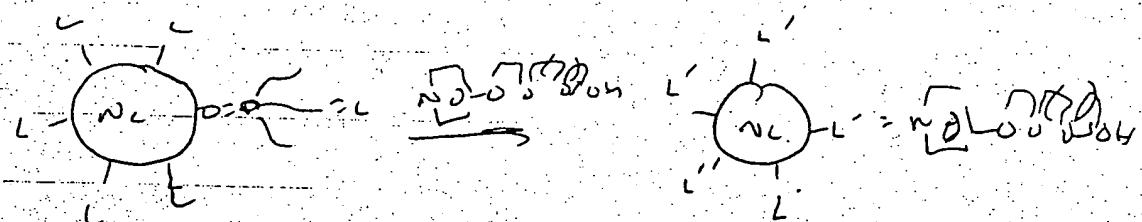
Reagents

1. TOPO covered NC   ~ 15 mg
2. $\underline{N_3}$-S........OH   320 mg
3. THF (dry)   3 mL }

Procedure

1. NC made as ~~usually~~ usual & washed w/ MeOH 3 times
2. dried over N_2 flow
3. redissolved in new ligand in THF and allowed to stand over head of N_2 overnight
4. distilled at ½ THF → precipitated w/ hexane → all NC precipitated
5. washed w/ hexanes → centrifuged → redissolved in H_2O